AD-A217 842

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE July 1980	3. REPORT TYPE AND DATES COVERED Final 6-19 July 1980	
4. TITLE AND SUBTITLE "NATO ADVANCED STUDY INSTITUTE FAST REACTIONS IN ENERGETIC SYSTEMS"			5. FUNDING NUMBERS 61102F 2308/A2
6. AUTHOR(S) Dr. C. Capellos			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Ioannina Ioannina, Greece			8. PERFORMING ORGANIZATION REPORT NUMBER AFOSR·TR· 90-0168
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR BLDG 410 BAFB DC 20332-6448			10. SPONSORING/MONITORING AGENCY REPORT NUMBER MIPR 80-00036
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT ... ... 350; ... ... unlimited.			12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

DTIC
S ELECTE
FEB 0 8 1990
D
D

14. SUBJECT TERMS			15. NUMBER OF PAGES 87
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT

Standard Form 298 (890104 Draft)
Prescribed by ANSI Std. 239-18
298-01

90 06 235

This Document Contains
Missing Page/s That Are
Unavailable In The
Original Document

OR are
Blank-pg?
that have
Been Removed

**BEST
AVAILABLE COPY**

NATO ADVANCED STUDY INSTITUTE
FAST REACTIONS IN ENERGETIC SYSTEMS
UNIVERSITY OF IOANNINA
IOANNINA-GREECE

ABSTRACTS
OF
FORMAL LECTURES
AND
CONTRIBUTED PAPERS

DIRECTOR: Dr. C. Capellos
NATO SCHOOL - Energetic Materials Division
LCWSL, ARRADCOM
Dover, New Jersey 07801
U.S.A.

C

ABSTRACTS OF CONTRIBUTED PAPERS   53

Organizing Committee

Professor M.I. Karayannis
University of Ioannina
Analytical Chemistry Laboratory
Ioannina, Greece

Dr. H. Schubert, Director
Institut fur Chemie der Treib und Explosivstoffe
7507 Pfinztal/Berghausen
Bei Karlsruhe Postfach 40
Karlsruhe, West Germany

Professor B.A. Thrush, F.R.S.
University of Cambridge
Department of Physical Chemistry
Lensfield Road
Cambridge, England

Dr. R.F. Walker, Chief
Energetic Materials Division
LCWSL, ARRADCOM
Dover, New Jersey 07801
U.S.A.

A. FAST REACTIONS AND ENERGY TRANSFER
    PROCESSES. ADVANCED DIAGNOSTICS.

ABSTRACTS

OF

FORMAL LECTURES

5

THEORY OF REACTION KINETICS

LECTURE I.   REACTION RATE THEORY.
LIQUID THEORY.

BY

PROF. H. EYRING
Dept. of Chemistry
The University of Utah
Salt Lake City, Utah 84112
U.S.A.

PROF. H. EYRING

Lecture I.   Reaction Rate Theory - Liquid Theory.

The development of activated complex (transition state theory) will be discussed critically. The sense in which equilibrium theory, activated complex theory and irreversible thermodynamics blend into each other will be discussed. The methods of handling a complex network of reactions will be outlined. The utility of potential energy surfaces in characterizing regular reactions and crossed beam experiments will be discussed as time allows.

A model of the liquid state will be developed. A single partition function for the solid liquid and vapor phases will be presented for argon with discussion of problems and in its extension to more complicated systems. The calculation for HCl and for water of their equilibrium and transport properties will be developed as time allows.

TIME RESOLVED ABSORPTION AND EMISSION SPECTROSCOPIES. ELECTRONICALLY EXCITED STATES.

LECTURE I.   PULSED LASER NANOSECOND, PICOSECOND AND SUBPICOSECOND SPECTROSCOPIES.

LECTURE II.   PHOTOPHYSICS OF ELECTRONICALLY EXCITED STATES

LECTURE III.   CHEMICAL REACTIVITY OF ELECTRONICALLY EXCITED STATES. CHARGE TRANSFER PROCESSES.

BY

DR. P. M. RENTZEPIS
Physical Chemistry Division
Bell Laboratories
600 Mountain Avenue
Murray Hill, New Jersey   07974
U.S.A.

ABSTRACT

We will consider the application of present available sources for the excitation of allowed and forbidden states by one, two, or multiple photons. The fate of these levels and the decay channels available will be examined under experimental conditions such as solvent, temperature and viscosity. Chemical reaction kinetics of electron and proton transfer reactions and the possibility of tunneling in biologically and chemically important reactions will be considered. Emphasis will be given to the latest methods of kinetic spectroscopy including picosecond absorption, emission and Raman spectroscopy as applied to the understanding of chemical reactions and energy transfer processes.

9

FAST IONIC REACTIONS IN SOLUTION

LECTURE I.   IONIZATION AND EXCITATION BY HIGH ENERGY
              ELECTRONS

LECTURE II.   PULSE RADIOLYSIS; FORMATION OF ORGANIC
              ANIONS AND CATIONS

LECTURE III. FAST REACTIONS OF ORGANIC MOLECULE IONS
              IN SOLUTION

BY

PROF. L. M. DORFMAN
Dept. of Chemistry
The Ohio State University
140 West 18th Avenue
Columbus, Ohio 43210
U. S. A.

L. M. DORFMAN

Lecture I. Ionization and Excitation by High Energy Electrons.

My lectures will center on the results of fast reaction studies of organic species in solution by means of the pulse radiolysis technique (1,2), a high energy electron impulse method. Accordingly, by way of introduction, in addition to a description of the technique, I will deal briefly with the nature of ionization and excitation by high energy electrons (0.1 to 20 MeV).

These electrons lose their energy in passing through matter by inelastic collisions with the orbital electrons in the absorber system. The energy loss per unit path length is described by the Bethe-Bloch (3) equations. Spatial inhomogeneities of energy deposition occur in the absorber system. If the absorber is a dilute solution, the energy deposition is almost exclusively in the molecules of the solvent rather than the solute, since the density of solvent molecules is several orders of magnitude greater than that of solute molecules in the solution.

Both ionization and electronic excitation occur, involving secondary electrons (having a continuous energy degradation spectrum) as well as the incoming primary electrons. The electronic excitation includes optically forbidden as well as allowed transitions, depending upon the energy of the electrons producing the excitation.

Examples of chemical systems illustrating these phenomena will be presented.

References:

1. M.S. Matheson and L.M. Dorfman, _Pulse Radiolysis_, M.I.T. Press, Cambridge, MA, (1969).

2. L.M. Dorfman, in "Techniques of Chemistry," Vol VI, Part 2, G.G. Hammes, Ed., Wiley-Interscience, New York, N.Y., p. 463, (1974).

3   H.A. Bethe and J. Ashkin, in "Experimental Nuclear Physics," Ed. E. Segre, Vol 2, Wiley, New York, p. 166 (1953).

L.M. DORFMAN

Lecture II.   Pulse Radiolysis: Formation of Organic Anions and
                 Cations

        The pulse radiolysis technique (1,2) is the high energy electron
impact analogue of flash photolysis in that a pulse of electrons (1μ
sec to 10 psec) is the energy perturbation on the system, which initi-
ates reaction. Measurement of the optical absorption in real time is
the most commonly used detection technique although other physical
properties of transient species have also been used in their detec-
tion. The experimental set-up for μsec and nsec detection will be
described, as will the techniques for psec time resolution (3,4).
Picosecond time resolution has been based on the use of an optical
delay line for the monitoring flash together with electronic signal
averaging. Some examples of measurement of specific chemical systems
will be shown.

        A good deal of work has been done on the kinetics of organic
molecule ions in solution. The mode of formation of organic radical
anions (5), radical cations, carbanions and carbocations (6) will be
discussed.

References:

1.   M.S. Matheson and L.M. Dorman, Pulse Radiolysis, M.I.T. Press,
      Cambridge, MA (1969).

2.   L.M. Dorfman, in "Techniques of Chemistry," Vol VI, Part 2, p.
      463, G.G. Hammes, Ed., Wiley-Interscience, New York, N.Y. (1974).

3.   M.J. Bronskill and J.W. Hunt, J. Phys. Chem., 72, 3762 (1968).

4.   M.J. Bronskill, W.B. Taylor, R.K. Wolff and J.W. Hunt, Rev. Sci.
      Intr., 41, 333 (1970).

5.   L.M. Dorfman, Acc. Chem. Res., 3, 224 (1970).

6.   L.M. Dorfman, R.J. Sujdak and B. Bockrath, Acc. Chem. Res., 9, 352
      (1976).

L. M. DORFMAN

Lecture III.   Fast Reactions of Organic Molecule Ions in Solution.

Fast reaction studies of aromatic radical anions, radical cations (1), carbanions and carbocations (2) have been carried out. Selected examples from these investigations will be presented. These include electron transfer reactions (1,3) from radical anions as the donor. Most recently our investigations have been concerned with the reactivities of carbocations (2,4,5,6). The reactivity of $PhCH_2^+$, Ph_2CH^+ and Ph_3C^+ with nucleophiles such as halide ions, alkylamines and alkenes has been determined.

References:

1. L.M. Dorfman, Acc. Chem. Res., 3, 224 (1970).

2. L.M. Dorfman, R.J. Sujdak and B. Bockrath, Acc. Chem. Res., 9, 352 (1976).

3. J.R. Brandon and L.M. Dorfman, J. Chem. Phys., 53, 3849 (1970).

4. R.J. Sujdak, R.L. Jones and L.M. Dorfman, J. Am. Chem. Soc., 98, 4875 (1976).

5. V.M. DePalma, Y. Wang and L.M. Dorfman, J. Am. Chem. Soc., 100, 5416 (1978).

6. Y. Wang and L.M. Dorfman, Macromol., 1, 63 (1980).

VIBRATIONALLY EXCITED STATES

LECTURE I.   KINETIC SPECTROSCOPY IN SHOCK WAVES

LECTURE II.   ACTIVATION AND DEACTIVATION OF
VIBRATIONALLY HIGHLY EXCITED STATES

LECTURE III.   UNIMOLECULAR PROCESSES OF
VIBRATIONALLY HIGHLY EXCITED STATES

BY

PROF. J. TROE
Institut fur Physicalische Chemie
der Universitat Gottingen
3400 Gottingen
Tammannstrasse 6
West Germany

J. TROE

Lecture I.   Kinetic Spectroscopy in Shock Waves.

Recent kinetic and spectroscopic experiments using optical detection methods in shock waves are discussed. Investigations of hot spectra for use in laser flash photolysis experiments are described. Recent studies of unimolecular reactions with one or two channels, which have used very sensitive vacuum UV techniques are reviewed.

References:

1.   E.F. Greene and J.P. Toennies, "Chemical Reactions in Shock Waves," Arnold, London (1964).

2.   A.L. Jaumotte, "Chocs et Ondes de Choc," Masson, Paris (1973).

J. TROE

Lecture II.   Activation and Deactivation of Vibrationally Highly
               Excited States.

Activation and deactivation of vibrationally excited states by collisions in thermal gases, by interaction with an intense IR laser field, and by the competition between both processes is discussed. Solution of the master equation, in analytical and numerical form, for the phenomena are described with experiments.

References:

1.   J. Troe, J. Chem. Phys, 66, 4745 (1977).

2.   J.E. Dove and J. Troe, Chem. Phys, 35, 1 (1978).

3.   M. Quack, Ber. Bunsenges, Physik. Chem. 83, 757, 1287 (1979).

LECTURE I.   DETECTION OF FREE RADICALS BY LASER
             MAGNETIC RESONANCE

LECTURE II.   MECHANISMS OF CHEMILUMINESCENCE IN GASES

BY

PROF. B. A. THRUSH
Department of Physical Chemistry
University of Cambridge
Lensfield Road
Cambridge, CB2 1EP
England

19

B.A. THRUSH

Lecture I.   Detection of Free Radicals by Laser Magnetic Resonance.

Apart from microwave spectroscopy which involves conditions far removed from those normally used to study free radical reactions in the laboratory, the rotational and vibration-rotation spectra of free radicals have been little studied until the recent advent of laser techniques. These techniques are related to electron paramagnetic resonance spectroscopy, but enjoy the advantage that the vibration-rotation and particularly the pure rotation spectra of free radicals are relatively strong. For many species individual rotational transitions can be tuned by as much as 1 cm^{-1} by a strong magnetic field (20kG). It is therefore possible to use the Zeeman effect to bring individual transitions into resonance with a fixed frequency laser. By studying the free radicals within the laser cavity, sensitivities as high as 10^{7} – 10^{10} radicals cm^{-3} can be achieved which make it possible to study the fastest reactions of free radicals. Applications to combustion chemistry and to atmospheric chemistry will be discussed as well as structural information obtained by this technique.

References:

1.   B.A. Thrush, "Laser Magnetic Resonance Spectroscopy of Free Radicals and Its Application to Atmospheric Chemistry," European Spectroscopy News, No. 20, 15 (1978).

2.   J.T. Hougen, "The Assignment of Molecular Infrared Spectra from a Laser Magnetic Resonance Spectrometer," J. Mol. Spec. 54, 447 (1975).

3.   K.M. Evenson, R.J. Saykally, R.F. Curl and J.M. Brown, "Far Infrared Laser Magnetic Resonance," XIV Int. Symp. on Free Radicals, Osaka (1979).

B.A. THRUSH

Lecture II.   Mechanisms of Chemiluminescence in Gases.

Although many elementary reaction processes release sufficient energy to generate electronically excited products, such species are rarely formed in transfer (metathetical) reactions, but are produced commonly in recombination reactions involving atoms. The mechanisms of various classes of chemiluminescent reaction will be discussed in terms of the potential surfaces involved and the rates of the luminescent and parallel nonluminescent processes. The application of chemiluminescence in the study of rapid, highly exoergic reactions will also be considered.

References:

1.   M.F. Golde and B.A Thrush, "Afterglows," Rep. Prog. Phys. 36, 1285 (1973).

2.   M.F. Golde and B.A. Thrush, "Chemiluminescence in Gases," Adv. Atom. Mol. Phys. 11, 361 (1975).

3.   T. Carrington and J.C. Polanyi, "Chemiluminescent Reactions," MTP Int. Review of Science, 9, 135 (1972).

21

FAST FREE RADICAL REACTIONS

LECTURE I.   FREE-RADICAL REACTIONS

LECTURE II.   CHAIN REACTIONS

BY

PROF. P. GRAY
School of Chemistry
The University of Leeds
Leeds, LS2 9JT
England

P. GRAY

Lecture I.   Free-Radical Reactions: Elementary Steps

1. Background

2. Fundamentals of kinetics briefly surveyed

3. Energetics of reactions: bond strengths

4. Free radical reactions: chemical classification;
    Association and dimerisation; addition; abstraction
    (of H, usually); H-atom 1000 to another radical;
    isomerisation; decomposition

5. Free radical reactions: kinetic classification

6. Initiation, propagation, termination and branching

7. The (quasi-) stationary state hypothesis

References:

Basic reading

1. J. Nicholas "Chemical Kinetics," Harper and Row, London (1976).

2. G.L. Pratt, "Gas Kinetics," John Wiley, London (1969).

More advanced reading

1. M.F.R. Mulcahy, "Gas Kinetics," Nelson, London (1973).

2. S.W. Benson, "Foundations of Chemical Kinetics," McGraw Hill, New
    York, NY (1960).

3. S.W. Benson, "Thermochemical Kinetics," 2nd Ed., J. Wiley, New
    York, NY (1960).

Reference books

1. D.L. Baulch, et al., "Evaluated Kinetic Data for High Temperature
    Processes,"

P. GRAY

Lecture II. Chain Reactions

1. Background: historical development

2. Characteristics of chain-reactions

3. Examples (of branched and unbranched chains)

4. Stationary-state treatment and ignition limits

5. Generalized, simplified treatments - stationary states

6. Interactions between chains

7. Nonstationary states

References:

Basic reading

1. F.G.R. Gumblett, "Kinetics of Chemical Chain Reactions," McGraw Hill, London (1970).

2. F.S. Dainton, "Chain Reactions", Methuen, London (1956).

More advanced reading

1. N.N. Semenov, Chemical Kinetics and Chain Reactions, Oxford (1935).

2. D.L. Baulch, et al., Evaluated Kinetic Data for High Temperature Processes.

B. SELF-SUSTAINED FAST REACTIONS

IN

ENERGETIC SYSTEMS

SELF-SUSTAINED FAST REACTIONS IN ENERGETIC SYSTEMS

LECTURE I.   THERMAL EXPLOSION THEORY

LECTURE II.   UNIFICATION OF THERMAL AND
               CHAIN-BRANCHING THEORY

BY

PROF. P. GRAY
School of Chemistry
The University of Leeds
Leeds, LS2 9JT
England

29

P. GRAY

Lecture I.   Thermal explosion theory

    1.   Background and aims

    2.   Semenov treatment of steady states and criticality for homo-
geneous systems

    3.   Critical self-heating, ignition limits

    4.   Heterogeneous systems: steady states, ignition and extinction

    5.   Nonsteady states

    6.   Examples: real systems

References:

Basic reading

1.   M.F.R. Mulcahy, "Gas Kinetics," Nelson, London (1973).

More advanced reading

1.   D.A. Frank-Kamenetskii, "Diffusion and Heat Transfer in Chemical
Kinetics," 2nd ed, Plenum Press, New York, NY (1969).

2.   P. Gray and P.R. Lee, "Thermal Explosion Theory," in Vol. 2 of
Oxidation and Combustion Reviews, Elsevier (1967).

P. GRAY

Lecture II.   Unification of Thermal and Chain-Branching Theory

1. Background - isothermal aspects

2. Interactions of branching and self-heating: phase plane
    Singular points and stationary states
    Limiting cases
    Can oscillations occur?

3. Oxidation of hydrocarbons - complexity

4. Thermokinetic interpretations

5. Modern experimental work

References:

Basic reading

1. M.F.R. Mulcahy, "Gas Kinetics," Nelson, London (1973).

2. P. gray, "Oscillatory Phenomena in Combustion," 16th Symposium
    (Int) on Combustion, Pittsburgh, p. 919 (1977).

More advanced reading

1. B.F. Gray, Vol 1 of Gas Kinetics (London Chem Soc. Specialist
    Periodical Report) (1975).

2. P. Gray and M.E. Sherrington, Vol 2 of Gas Kinetics (London Chem.
    Soc. Specialist Periodical Report) (1977).

FAST MOLECULAR PROCESSES IN COMBUSTION - FLAME CHEMISTRY

LECTURE I.   EXPERIMENTAL METHODS IN FLAME KINETICS

LECTURE II.   MAIN FEATURES OF COMBUSTION REACTIONS IN FLAMES

LECTURE III. DETAILED MECHANISMS OF SOME FLAMES

BY

PROF. P.J. VAN TIGGELEN
Laboratoire de Physicho-Chimie
de la Combustion
Universite Catholique de Louvain
Louvain-la-Neuve
Belgium

33

P.J. VAN TIGGELEN

Lecture I.   Experimental Methods in Flame Kinetics

1. Introduction - Earlier attempt of chemical kinetics in flames

2. Use of low pressure premixed laminar flames

3. Sampling techniques for concentration measurements

4. Temperature profiles

5. Mass spectrometric analysis

6. Calibrating procedure for quantitative measurements

7. Superimposition of profiles

References:

1.   R.M. Fristrom and A.A. Westenberg: Flame Structure, McGraw Hill (1965)

2.   C.P.Fenimore: Chemistry in Premixed Flames - The International Encyclopedia of Physical Chemistry and Chemical Physics, Topic 19, Vol. 5, Pergamon Press (1964).

P.J. VAN TIGGELEN

Lecture II. Main Features of Combustion Reactions in Flames

1. Review of physical processes in flames

2. Reduction of experimental data

3. Net reaction rate of individual species

4. Stoichiometric requirements and equilibrium composition

5. Partial equilibrium and reactions in the postcombustion zone

6. Pool flux concept

7. Decomposition reaction

8. An example: Nitrous oxide-hydrogen flame

References:

1. R.M. Fristrom and A.A. Westenberg, Flame Structure, McGraw Hill (1965).

2. J.O. Hirschfelder, Ch. E. Curtiss and R.P. Bird, "Molecular Theory of Gases and Liquids," J. Woley, New York, N.Y. (1964).

3. . Kaskan and G. Schott, Comb and Flame, 6, p. 73 (1962).

4. . Peeters and G. Mahnen, 14th Symp (Internat.) on Combustion, p. 133 (1973).

P.J. VAN TIGGELEN

Lecture III. Detailed Mechanisms of Some Flames

1. The hydrogen-oxygen system

2. The rate constant of CO + OH elementary step

3. Methane flames

4. Acetylene and ethylene flames

5. Methanol as a fuel

6. Formaldehyde consumption in flames

7. Inhibition processes in flames

References:

1. J. Vandooren and P.J. Van Tiggelen, XVIth Symp. (Internat.) on Combustion, p. 1133 (1977).

2. G. Dixon-Lewis and R.J. Simpson, Ibid, p. 1117.

3. J.C. Biordi, C.P. Lazazzara and J.F. Papp, Ibid, p. 1097.

COHERENT ANTI-STOKES RAMAN SCATTERING

LECTURE I.   THEORY

LECTURE II.   PRACTICAL MEASUREMENTS

LECTURE III. RESONANT CARS

BY

DR. J. P. TARAN
Office National d'Etudes
et de Recherches
Aérospatiales (ONERA)
92320 Chatillon
France

J. P. TARAN

Lecture I. Theory

For a clear understanding of the main properties of Coherent
Anti-Stokes Raman Scattering (CARS), the theory of the effect is pre-
sented thoroughly. A quantum mechanical derivation of the nonlinear
source polarization generated within the medium by the pump waves is
first given. The anti-Stokes wave generation is then created through
Maxwell's equations.

All the important spectral properties are deduced from the
expression for the source polarization, while wave-vector matching
conditions, spatial resolution, and signal conversion efficiency are
obtained from the wave equation of the signal. One can also infer the
important rules of energy transfer by considering the set of wave
equations for the pump fields.

Finally, the applicability of CARS to the delicate probing of
gaseous media undergoing chemical reactions is discussed.

J. P. TARAN

Lecture II. Practical Measurements

An overview of past achievements of CARS in the probing of gas
phase media is first given. We also discuss the state of the art in
spectral resolution, measurement accuracy, spatial resolution and
detectivity. The latter two have recently been improved substantially
thanks to the introduction of BOXCARS and polarization cancellation of
the background.

The CARS spectrometer in use at ONERA is described and its per-
formance given. The results obtained lately in practical combustors
and low pressure discharges are commented.

39

J.P. TARAN

Lecture III. Resonant CARS

The study of resonant CARS was undertaken several years ago because large improvements in the detectivity of trace species then were expected. It now appears that this technique offers two major areas of applications:

--sensitive detection of trace species,

--analysis of Raman and absorption properties of molecules.

The latter field is an extremely promising area of research.

We described the theory of resonance CARS spectroscopy, its main applications, the experimental work done at ONERA in I_2, and the fundamental conclusions of our theoretical analysis of the effect in the Doppler regime.

References:

1. P. Regnier, F. Moya, and J.P.E. Taran, AIAA Journal 12, 826 (1974).

2. J.N. Nibler and G.V. Knighten, "Coherent Anti-Stokes Raman Spectroscopy," in Topics in Current Physics," Ed. by A. Weber, Springer Verlag, New York (1977).

3. S. Druet, B. Attal, T.K. Gustafson and J.P. Taran, Phys. Rev, A18, 1529 (1978).

4. N. Bloembergen, H. Lotem and R.T. Lynch, Indian J. Pure Appl. Phys., 16, 151 (1978).

5. S. Druet, J.P. Taran and Ch. J. Borde, J. de Physique, 40, 819 (1979); addendum, ibid 41, 183 (1980).

6. B. Attal, M. Pealat and J.P. Taran, AIAA paper n° 80-0282, presented at the AIAA 18th Aerospace Sciences Meeting, Pasadena, CA, January 14-16, 1980.

7. A.C. Eckbreth, R.J. Hall and J.A. Shirley, AIAA paper 79-0083, presented at the AIAA 17th Aerospace Sciences Meeting, New Orleans, LA, January 15-17 1979.

8. G.L. Switzer, L.P. Goss, W.M. Roquemore, R.P. Bradley, P.W. Schreiber and W.B. Roh, AIAA paper 80-0353, presented at the AIAA 18th Aerospace Sciences Meeting, Pasadena, CA, January 14-16, 1980.

ELECTRONIC AND VIBRATIONAL ENERGY EXCHANGE IN MOLECULES AND IN CONDENSED PHASES

LECTURE I.   INTRAMOLECULAR AND INTERMOLECULAR
               DYNAMICS. REACTIVE PROCESSES.
               PREDISSOCIATION.

LECTURE II.   NONREACTIVE MOLECULAR PROCESSES.
               ELECTRONIC RELAXATION. INTRAMOLECULAR,
               VIBRATIONAL ENERGY FLOW.

LECTURE III.   COHERENT OPTICAL EFFECTS. RELAXATION AND
               DEPHASING IN CONDENSED PHASES. SOME
               PROBLEMS IN BIOPHYSICS.

BY

PROF. J. JORTNER
Institute of Chemistry
Tel-Aviv University
61390 Ramat-Aviv
Tel-Aviv, Israel

J. JORTNER

References:

1. J. Jortner, S.A. Rice and R.W. Hochstrasser, in Advances in Photochemistry, Vol. 7, Ed. by W.A. Noyes, J.N. Pitts and G. Hammond, Wiley, New York, N.Y. (1969).

2. J. Jortner, J. Chim. Phys. special issue "Transitions Non-radiatives dans les Molecules," p. 1 (1970).

3. J. Jortner and S. Mukamel, in The World of Quantum Chemistry, Proc. First Intnl Congress on Quantum Chemistry, Menton, France, July 1973, Reidel Publishing Company, p. 145 (1974).

4. J. Jortner and S. Mukamel, in MTP International Review of Science, Vol. 13, Eds. A.D. Buckingham and C.A. Coulson, Butterworth, London (1976).

5. J. Jortner and R.D. Levine, in Molecular Energy Transfer, Eds. R.D. Levine and J. Jortner, Wiley, New York, N. Y., p. 1 (1975).

6. J. Jortner and S. Mukamel, in Molecular Energy Transfer, Eds. R.D. Levine and J. Jortner, Wiley, New York, p. 178 (1975).

7. J. Jortner, B. Raz and O. Cheshnovsky, in Molecular Energy Transfer, Eds R.D. Levine and J. Jortner, Wiley, New York, N.Y., p. 237 (1975).

FAST REACTIONS IN DISPERSED HETEROGENEOUS ENERGETIC SYSTEMS

LECTURE I.   DESCRIPTION AND FORMULATION OF THE PROBLEM

LECTURE II.   BLAST WAVE INITIATION OF HETEROGENEOUS DETONATION

LECTURE III.   BLAST WAVE INITIATED DETONATION; LIQUID FUELS AND DUSTS

BY

PROF. J. A. NICHOLLS
Department of Aerospace Engineering
The University of Michigan
Ann Arbor, Michigan 48109
U.S.A.

J. A. NICHOLLS

Lecture I. Description and Formulation of the Problem.

Practical cases where fuel is dispersed in the atmosphere so as
to form an unconfined combustible cloud are described. Soft ignition
versus blast wave initiation is discussed. An outline of the rest of
the three lectures, which pertain to blast wave initiation, is pre-
sented. The characteristics of blast waves and detonation waves for
the homogeneous case (all gaseous) are described. The blast wave
initiation of detonation for the homogeneous case, including an out-
line of the theoretical development, is outlined. Differences that
arise when the fuel is in the form of liquid drops are discussed.

References:

1.   J.H.S. Lee, "Initiation of Gaseous Detonations," Ann. Rev. Phy.
     Chem., 28, pp. 75-104 (1977).

2.   J.A. Nicholls, M. Sichel, R.S. Fry, and D.R. Glass, "Theoretical
     and Experimental Study of Cylindrical Shock and Heterogeneous
     Detonation Waves," Acta Astronautica, 1, pp. 385-404 (1979).

3.   V. Korobeinikov, V., "The Problem of Point Explosion in a
     Detonating Gas," Astronautica Acta, 14, pp. 411-419 (1969).

4.   G.G. Chernyi and V.A. Levin, "Asymptotic Laws of Behavior of
     Detonation Waves," P.M.M., 31, pp. 393-405 (1967).

5.   M. Sichel, "A Simple Analysis of the Blast Initiation of Detona-
     tions," Acta Astronautica, 4, pp. 3-4 (1977).

6.   L.I. Sedov, Similarity and Dimensional Methods in Mechanics, 4th
     Edition, Academic Press, New York, N.Y. (1959).

J. A. NICHOLLS

Lecture II. Blast Wave Initiation of Heterogeneous Detonation

The properties of heterogeneous detonation, as they differ from the homogeneous case, are discussed. Analytical and experimental results are then presented and discussed which relate to the shattering and ignition of liquid fuel drops. An experimental facility for studying the blast wave initiation of detonation in unconfined cylindrical clouds is described. Experimental results are presented which show the decay of the blast wave in gases as well as through a spray and the blast wave initiation of detonation in homogeneous mixtures.

References:

1. F.A. Williams, Detonations in Dilute Sprays, Progress in Astronautics and Rocketry, 6, Academic Press, New York, N.Y. pp. 99-114 (1962).

2. E.K. Dabora, K.W. Ragland, and J.A. Nicholls, "A Study of Heterogeneous Detonations," Astronautica Acta, 12, pp. 2377-2388 (1966).

3. K.W. Ragland, E.K. Dabora and J.A. Nicholls, "Observed Structure of Spray Detonations," Phys. Fluids, 11, pp. 2377-2388 (1968).

4. E.K. Dabora, K.W. Ragland and J.A. Nicholls, "Drop Size Effect in Spray Detonations," 12th International Symposium on Combustion, The Combustion Institute, Pittsburg, PA, pp. 19-26 (1969).

5. A.A. Ranger and J.A. Nicholls, "Aerodynamic Shattering of Liquid Drops," AIAA J., 7, pp. 285-290 (1969).

6. B.D. Fishburn, "Boundary Layer Stripping of Liquid Drops Fragmented by Taylor Instability," Acta Astronautica, 1, pp. 1267-1284 (1976).

7. C.W. Kauffman and J.A. Nicholls, "Shock Wave Ignition of Liquid Fuel Drops," AIAA J., 9, pp. 880-885 (1971).

J.A. NICHOLLS

Lecture III. Blast Wave Initiated Detonation; Liquid
              Fuels and Dusts

Experimental data relative to the blast wave nitiation of heterogeneous detonation (liquid fuel drops) is presented and discussed. Streak photography, high framing speed photography, pressure measurement, and velocity data are included. Aspects studied include a number of fuels, the role of fuel volatility, the case with a region devoid of fuel, and the addition of a more sensitive fuel. Attention is given to the proper definition of an induction zone for a heterogeneous system and how this agrees with the theory. The case for dusts is also discussed. The differences in the mechanism involved is described. Results are presented for a metal dust, coal dust, grain dust, and feed. Summarizing statements of the three lectures are included.

References:

1. Z.M. Gabrijel and J.A. Nicholls, "Cylindrical Heterogeneous Detonation Waves," Acta Astronautica, 5, pp. 1051-1061 (1978).

2. R. Bar Or, M. Sichel and J.A. Nicholls, "The Propagation of Cylindrical Detonations in Monodisperse Sprays," to be presented at the 18th International Symposium on Combustion, The University of Waterloo, Ontario, Canada, August 1980.

3. A.A. Borisov, B.E. Gel'fand, S.A. Gubin, S.M. Kogarko and A.L. Podgrebenkov, "The Reaction Zone of Two-Phase Detonations," Astronautica Acta, 15, pp. 411-417 (1970).

4. P.L. Lu and N. Slagg, "Chemical Aspects in the Shock Ignition of Fuel Drops," Acta Astronautica, 1, pp. 1219-1226 (1976).

5. P.L. Lu, N. Slagg, B.D. Fishburn, and P.P. Ostrowski, "Relation of Chemical and Physical Processes in Two Phase Detonation," Paper presented at the 6th International Colloquium on Gas Dynamics of Explosion and Reactive Systems, Stockholm, Sweden, August 1977.

6. M. Sichel and C.C. Yeu, "The Role of Droplet Breakup in the Induction Zone of Two-Phase Detonation," was presented at the Eastern Section of the Combustion Institute, Atlanta, GA, November 1979.

7. T.W. Fox, C.W. Rackett and J.A. Nicholls, "Shock Wave Ignition of Magnesium Powders," Shock Tube and Shock Wave Research, Proc. 11th Int'l Symposium on Shock Tubes and Waves, Univ. Wash. Press, pp. 262-268 (1978).

J. A. NICHOLLS

8. C.W. Kauffman, P. Wolanski, E. Ural, J.A. Nicholls and R. Van
    Dyk, "Shock Wave Initiated Combustion of Grain Dust," presented
    at the Symposium on Grain Dust, U.S. Grain Marketing Research
    Lab., Manhattan, KS, October 2-4, 1979.

GASDYNAMICS OF FAST REACTIONS

LECTURE I.   FUNDAMENTAL MODES OF COMBUSTION; CONSTANT
              VOLUME COMBUSTION AND THE CLASSICAL
              STRUCTURE OF LAMINAR FLAMES AND DETONATIONS.

LECTURE II.   HYDRODYNAMIC STABILITY AND TURBULENCE EFFECTS
              OF FLAME PROPAGATION.

LECTURE III. MECHANISMS OF DETONATIVE COMBUSTION; THE ROLE
              OF TRANSVERSE ACOUSTIC WAVES.

LECTURE IV.   MECHANISMS OF FLAME ACCELERATION AND TRANSITION
              FROM DEFLAGRATION TO DETONATION.

BY

PROF. J.H. LEE
Department of Mechanical Engineering
McGill University
Montreal, Canada

ABSTRACT

The rate of uniform burning of a finite volume of homogeneous reactive gas mixtures depends on the kinetic rate constants of the detailed elementary reactions. However, if the reaction is initiated locally the overall combustion rate will depend on the speed of propagation of the reaction front which depends on the particular mode of combustion itself, that is deflagration or detonation. Significant gasdynamic effects can be generated in fast exothermic systems and as a result the reaction rate (i.e., velocity of the combustion front) can be strongly influenced. The present lectures discuss the inter-coupling between the reaction rate with the gasdynamic flow structure generated as a result of the exothermic reactions.

DETONATION KINETICS

LECTURE I. DEFLAGRATION TO DETONATION THEORY

BY

PROF H. EYRING
The University of Utah
Dept. of Chemistry
Salt Lake City
Utah 84112
U.S.A.

PROF. H. EYRING

Lecture I.   Deflagration to Detonation Theory

An important unfinished problem is the theory of transition from
deflagration to detonation DDT. The understanding of this problem is
critical for the safe handling of explosives. Some of the successes
of deflagration and detonation theory are outlined. For detonation to
occur in a cylindrical explosive, for example, one must remember that
as a shock wave moves into cold explosive the shock loses energy and
is dying out. Behind a developed wave front there is a succession of
increasingly exothermic reaction surfaces rising to a maximum at the
Chapman-Jouguet surface where rarefaction begins. A sufficiently
sharp blow or an intense beam of laser light falling on unreacted
explosive generates this type of structure which travels through the
material as a self supporting shock wave. How to avoid forming such
structures which will grow into travelling self supporting waves has
many aspects. Here we consider (a) starvation kinetics which arises
from a change of reaction mechanism due to the sudden introduction of
unburned material into a hot environment. As the gradient from
unburned to burned material rises a situation develops where the
fastest way to get energy into the bond that breaks is not directly
from translation to this bond but through a reservoir which readily
communicates energy. This shifts the developing bottle neck of ener-
gizing the molecule (starvation kinetics) to a new pathway with inter-
esting consequences; (b) turbulence promotes initiation of detonation
by sharpening the concentration and temperature gradients between
unburned and burned materials; (c) the dependence of shock wave veloc-
ity, due to momentum loss out the side is related to the diameter of
the explosive. (d) The curvature of the wave front is related to drag
of telescoping cylinders on the central axis of the cylindrical explo-
sive.

ABSTRACTS

OF

CONTRIBUTED PAPERS

THE APPLICATION OF ADVANCED OPTICAL TECHNIQUES TO THE STUDY OF FAST ENERGETIC REACTIONS

W.L. FAUST, L.S. GOLDBERG, T.R. ROYT,
P. SCHOEN, J.M. SCHNUR
Naval Research Laboratory
Washington, D.C. 20375 U.S.A.
and
B. CRAIG* AND R. WEISS
Georgetown University
Washington, D.C., U.S.A.

ABSTRACT

The diagnostic technique of short-pulse transient absorption spectroscopy enables investigation of very fast photo-initiated reactions in gaseous and condensed media, regimes where primary reaction rates are high and secondary reactions can ensue very quickly. The primary product species that arise from decomposition can be identified through their characteristic absorption spectrum and their kinetic behavior can be followed with picosecond time resolution. This allows one to view the earliest microscopic processes essential to the reaction and to trace the reaction pathways through subsequent processes as far as possible. We have carried out such studies on photolysis of the nitromethane molecule where we have identified the NO_2 radical as a primary reaction product and have determined its kinetics of formation. The essential similarity of the HMX molecule, containing as it does the reactive NO_2 groups, suggests a very productive investigation by this approach.

The laser apparatus developed at NRL for these studies utilizes a modelocked Nd:YAG oscillator/amplifier system. Photoinitiation is performed with an intense short UV pulse derived by harmonic generation from an amplified 1.06 µm pulse of 30 picoseconds duration. The 1.06 µm pulse is also used to produce a white-light continuum probe pulse which then interrogates the spectrum of the photo-produced products. This spectrum is recorded in dual-beam form on a vidicon multichannel analyser system and is studied as a function of probe delay time.

The second diagnostic technique to be discussed is that of laser induced fluorescence. Under favorable circumstances this approach is capable of following extremely small quantities of

B. CRAIG

Intermediate species from a reaction, both spatially and temporally. A synchronous mode locked dye laser is tuned to probe an absorbing transition from a suspected product species, and its subsequent fluorescent emission serves as a signal of its presence. Species such as CH, C_2, NH, and others can be detected to concentrations as low as 10^7-10^8 species per cubic centimeter. Currently this technique is being applied to the study of the photolysis of ketene, and the subsequent observation of CH_2.

The potential of these techniques to be applied to other problems associated with fast energetic materials will also be discussed.

EXCESS VIBRATIONAL ENERGY EFFECTS IN THE LOWEST TRIPLET STATE OF A MEDIUM SIZE MOLECULE

H. STAFAST
Physical Chemistry Institute
University of Zurich Irchel
Winterthurer Str., 190, CH-8057, Zurich

ABSTRACT

Propynal, $HC \equiv C-CHO$, is a medium size molecule with a singlet-triplet (S_1-T_1) energy gap of 2000 cm^{-1} and a triplet vibrational state density of about $0.5/cm^{-1}$ at the zero vibrational level of the S_1 state. Its phosphorescence emission spectrum and excited state decay kinetics are useful probes for studying excess vibrational energy effects. Thermalized T_1 molecules of 300K were produced by N_2 laser irradiation in the 1 torr region. Subsequent TEA CO_2 laser excitation yielded triplet molecules in the energy region of S_1 vibrational levels. With the experimental findings including those of the α-deuterated compound important information is gained about the coupling between the T_1, S_1, and S_0 state levels at different vibrational temperatures.

References:

1. T.P. Cotter, W. Fuss, K.L. Kompa, and H. Stafast, Infrared Vibrational Superexcitation, Opt. Comm. 18, 220 (1976).

2. H. Stafast, W.E. Schmid and K.L. Kompa, Absorption of CO_2 laser pulses at different wavelengths by ground-state and vibrationally heated SF_6, Opt. Comm. 21, 121 (1977).

3. H. Stafast, J. Opitz, and J.R. Huber in "IR Photochemistry in an Electronically Excited State," in Laser-Induced Processes in Molecules, edit. by K.L. Kompa and S.D. Smith, Springer Series in Chemical Physics 6, Springer-Verlag (1979).

4. H. Stafast, J. Opitz, U. Brühlmann, and J.R. Huber, Perturbation of the phosphorescence decay of propynal upon TEA CO_2 laser irradiation, J. Mol. Struct., in print.

AN OBSERVATION OF COLLISION-FREE, INTRAMOLECULAR VIBRATIONAL REDISTRIBUTION IN S_1 p-FLUOROTOLUENE

D.A. DOLSON, C.S. PARMENTER, AND B.M. STONE*
Department of Chemistry
Indiana University
Bloomington, IN 47401
U.S.A.

ABSTRACT

Vibrational redistribution with $c_{vib} = 2000$ cm^{-1} in the S_1 state of p-fluorotoluene vapor has been followed by observation of the time evolution of electronic fluorescence spectra after initial S_1 preparation. A chemical timing technique using an efficient electronic state quencher at high gas pressures has extended the time resolution to a few picoseconds. Kinetic analysis shows the redistribution time to be about 10 picoseconds.

The presence or absence of redistribution during the lifetime of the S_1 state can be detected by ordinary collision-free single vibronic level fluorescence. The spectral changes in the SVL fluorescence as excitation climbs the S_1 ladder shows that redistribution first occurs at remarkably low (ca. 1500 cm^{-1}) vibrational energies.

References:

1. K.Y. Tang, PhD thesis, Dept. of Chem., Indiana University, Bloomington, IN.

2. R.G. Brown and D. Phillips, Journal of the Chemical Society, Faraday Trans. II, 70, p. 630 (1974).

3. R.P. Steer, M.D. Swords, and D. Phillips; Chemical Physics, 34, pp. 95-102 (1978).

4. R.A. Coveleskie, D.A. Dolson, and C.S. Parmenter, Journal of Chemical Physics (in press).

TEMPERATURE MEASUREMENTS IN SHOCKED ENERGETIC MATERIALS BY TIME-RESOLVED INFRARED RADIOMETRY

W. G. VON HOLLE
Lawrence Livermore Laboratory, L-324
P.O. Box 808
Livermore, CA 94550
U.S.A.

ABSTRACT

The infrared emission from several explosives, propellants and inerts was measured in the region from 2-5.5 micrometers using two radiometers with about 400 ns rise time. Two basically different types of projectile-impact experiments were performed on a 102 mm gas gun. In one, emission from the down-stream face of the shocked material was observed in vacuum; in the other, the down-stream face was confined by a shock-impedance matched, infrared transmitting window. In the latter case, the temperature of the material was measured as chemical energy release was allowed to occur under increasing pressure at the interface.

Results of the bare-charge experiments indicate a heterogeneously heated surface, and hot spot temperatures were inferred from the radiance histories. The peak temperatures were found to increase monotonically with increasing input stress and to correlate with the physical and chemical properties of the shocked materials. The temperature histories of shock bare charges can also be used to extract other approximate hot spot parameters. For example in PBX-9404, with the help of a simple model, the hot spot temperature decay is consistent with a hot spot radius of one micron. The temperature decay can also be used to derive the fraction of the material reacted in the shock front.

Using the technique of confinement of the material on the down-stream face, a single experiment yields single-band and "color" temperature histories of the material. The "color" or two-band temperature is inherently independent of the hot area of a heterogeneous source, and this has made it possible to calculate the approximate fraction of the surface which is heated and to follow its evolution as the pressure increases. This heated fraction is sensitive to input stress, and its measurement is a promising new tool for the study of energetic materials under dynamic conditions.

ENERGY RELAXATION IN LIQUID TETRACHLORIDES IN EQUILIBRIUM

TH. DORFMÜLLER* AND D. SAMIOS
Physical Chemistry Dept.
University of Bielefeld
48 Bielefeld Postfach 8640
West Germany

ABSTRACT

The relaxation of the vibrational energy in a liquid is mainly determined by the number of collisions a molecule undergoes with its neighbours and by a transition probability. The experimental relaxation times as obtained by the analysis of the Brillouin light scattering spectra is described in the frame of an isolated binary collision theory. The results for CCl_4, $SiCl_4$, $SnCl_4$, and the respective mixtures are given and analysed in terms of structural properties of the liquids and the anisotropy of intermolecular potential.

SHOCK PROPAGATION AND DISSOCIATION IN SIMPLE AND COMPLEX ONE-DIMENSIONAL SYSTEMS

J.R. HARDY*
University of Nebraska
Lincoln, NE, U.S.A.
and
A.M. KARO
Lawrence Livermore National Laboratory
Livermore, CA, U.S.A.

ABSTRACT

The study of shock propagation in condensed matter lies in an interdisciplinary area between engineering, chemistry, and physics where the application of computer molecular dynamics can make valuable contributions. Adding to the upsurge of interest in the properties of shocks in condensed media has been a growing awareness of the need to understand the microscopic details of shock-initiation processes, and how shock loading may initiate chemical reactions in energetic materials. At the same time the theoretical understanding of the propagation of strong disturbances in discrete media has advanced rapidly over the past few years. This progress has been made possible both by computer simulations and by a new ability to understand the results of those simulations in analytic terms. Specifically, the concept of solitary waves and solitons in discrete systems is now well-defined, and many previously puzzling results of computer simulations of shock loading find a natural interpretation in terms of the generation of solitary waves or near-soliton disturbances.

In the first lecture we lay the groundwork for the application of computer molecular dynamics to the study of shock propagation in both inert and reactive systems. A brief historical review will be followed by a thorough treatment of shock development and shock characteristics as they are influenced by such factors as the nature of the interatomic potential, the type of loading (i.e., the initial conditions used to generate large-amplitude disturbances), and the structure of the chain itself. Both inert and reactive chains will be considered, and our examples will progress from simple monatomic chains to complex "polyatomic" structures. The solitary-wave or soliton-like features of the propagating distrubance will be examined. A short computer-generated movie will illustrate some of the main points of the lecture.

SHOCK PROPAGATION AND DISSOCIATION IN PERFECT AND STRUCTURALLY IMPERFECT MONATOMIC TWO-DIMENSIONAL SYSTEMS

A. M. KARO*
Lawrence Livermore National Laboratory
Livermore, CA, U.S.A.
and
J.R. HARDY
Department of Physics and Astornomy
University of Nebraska
Lincoln, NE 68588
U.S.A.

ABSTRACT

In the second lecture we will consider two-dimensional systems. The two-dimensional monatomic case represents a model system that can usefully be studied in detail, and we will see that much physical insight can be gained from a series of carefully-designed computer experiments. Later, additional complexity will be introduced when we treat 2D and 3D molecular structures.

We will review the behavior of shocks in both perfect and structurally imperfect systems; their stability and their interaction with defects and surfaces. We ask whether or not there exist non-thermal or dynamic processes by means of which the energy localized in the shock front may initiate chemical reactions in energetic materials: driving the system from a metastable initial configuration over an energy barrier toward a more stable ensemble of products. In addition to spatial rearrangements which may initiate reaction in energetic materials we have also a general disruption of the lattice occuring in the neighborhood of imperfections such as inclusions, voids, and grain boundaries, and from the spalling of surface material. These processes give rise to energetic atomic and molecular fragments which, in a real system, may also play an important role in the ensuing chemical reactions.

To illustrate these points we will consider the interaction of a shock wave with various point imperfections and with line imperfections such as edge dislocations and grain boundaries. We will see that the results of the calculations vary markedly and depend strongly on the nature and strength of binding and on the mass of the point imperfection. We will show that, although direct energy transfer from the shock to the normal modes of the perfect

A.M. KARO

lattice may indeed be a low-order process within the pure bulk
material, the role played by imperfections and irregularities in
providing a channel for coupling with the energy localized in the
shock front may be quite significant, particularly when near one of
the surfaces.

Finally, in this second lecture we will consider model
lattices bonded by potentials that simulate the effect of an
exothermic chemical reaction following bond rupture. This
particular model two-body potential can be considered formally as a
mathematical expression constructed so as to allow bond breaking to
be exothermic, and informally as a simulation that permits
identification of the displacement coordinates of the dynamical
calculation with the reaction coordinates of a chemically reacting
system.

A second computer-generated movie will be used to illustrate
the topics discussed in this lecture.

KINETIC APPLICATIONS OF ELECTRON PARAMAGNETIC RESONANCE SPECTROSCOPY. QUANTUM-MECHANICAL TUNNELING IN AN INTERMOLECULAR HYDROGEN ATOM ABSTRACTION

V. MALATESTA* AND K.U. INGOLD
Division of Chemistry
National Research Council of Canada
Ottawa, Canada K1A 0R6

ABSTRACT

The rate constants for hydrogen atom abstraction by bis-trifluoromethyl nitroxide from toluene in chlorofluorocarbon solvents have been measured by kinetic EPR spectroscopy from 327 to 121 K. An Arrhenius plot of this data is strongly curved. It is concluded that quantum-mechanical tunneling plays an important role in the reaction at low temperatures. Calculations using an Eckart barrier yield a barrier height of 14.0 kcal/mol. The O-H bond strength in $(CF_3)_2NOH$ has been found to be 82.6 kcal/mol using an EPR equilibrium technique. The hydrogen atom abstraction from toluene is therefore probably slightly endothermic. Some measurements with toluene-d_8 illustrate the problems which arise when trying to observe anticipated large deuterium kinetic isotope effects in intermolecular reactions in solution.

RAPID REACTION AND QUENCHING OF FREE RADICAL REACTIONS INITIATED BY AN INFRARED LASER PULSE. COMPUTER MODEL OF INHOMOGENEOUS RAPID REACTIONS

N.C. PETERSON*, W. BRAUN, T. ISHII
National Bureau of Standards
Washington, DC
U.S.A.

ABSTRACT

Methyl radicals are generated by multiple photon dissociation of acetone in a small volume. The temperature rises rapidly to 2000 K and high temperature reactions take place. Rapid expansion quenches the high temperature reactions in times less than 10^{-5}s. Coupling of the chemical reactions with hydrodynamics is required for a computer model consistent with experimental data.

FAST REACTIONS IN DETONATING HOMOGENEOUS EXPLOSIVES

C.L. MADER
Los Alamos Scientific Laboratory
P.O. Box 1663
Los Alamos, NM
U.S.A.

ABSTRACT

An explosive that does not have density discontinuities such as a gas, liquid, or single crystal is called a homogeneous explosive.

The time dependent behavior of the flow in the reaction zones of the detonating homogeneous explosives, nitromethane, liquid TNT, and ideal gases, have been investigated using one- and two-dimensional Lagragian and Eulerian numerical hydrodynamics with Arrhenius chemical reaction and accurate equations of state.

The perturbed one- and two-dimensional Lagrangian and Eulerian calculations reproduce the analytical predictions of Erpenbeck regarding the stability of the ideal gas reaction zone in one and two dimensions and indicate that the stabilities of the reaction zones of nitromethane and liquid TNT are identical in one and two dimensions.

For significant ranges of values for the activation energy and of values for the amount of overdrive, the reaction zones advance in a pulsating manner, with the flow parameters in the reaction zone oscillating about their steady-state values.

References:

Basic

1. D.L. Chapman, "On the Rate of Explosion in Gases," Philosophical Magazine 47, 90 (1899).

2. Wildon Fickett and W.W. Wood, "Numerical Calculations of One-Dimensional, Unstable, Pulsating Detonations," Physics of Fluids 9, 903 (1966].

3. C.L. Mader, "Shock and Hot Spot Initiation of Homogeneous Explosives," Physics of Fluids 6, 375 (1963).

C.L. MADER

4.   J.J. Erpenbeck, "Stability of Idealized One-Reaction Detona-
     tions," Physics of Fluids 7, 684 (1964) and "Stability of
     Steady-State Equilibrium Detonations," Physics of Fluids 5,
     604 (1962).

Advanced

1.   W. Fickett, J.D. Jacobson, and G.L. Schott, "Calculated Pul-
     sating One-Dimensional Detonations with Induction Zone," AIAA
     Journal 4, 514 (1972).

2.   B. Hayes, "Electrical Measurements in Reaction Zones of High
     Explosives," Tenth International Symposium on Combustion,
     Cambridge, England (1964).

3.   B.G. Craig, "Measurements of the Detonation-Front Structure in
     Condensed-Phase Explosives," Tenth International Symposium on
     Combustion, Cambridge, England (1964).

4.   W.C. Davis, B.G. Craig, and J.B. Ramsay, "Failure of the
     Chapman-Jouguet Theory for Liquid and Solid Explosives,"
     Physics of Fluids 8, 2169 (1965).

5.   C.L. Mader, Numerical Modeling of Detonations, University of
     California Press (1979).

67

FAST THERMAL REACTIONS IN HOMOGENEOUS EXPLOSIVES

C.L. MADER
Los Alamos Scientific Laboratory
P.O. Box 1663
Los Alamos, NM
U.S.A.

ABSTRACT

Bulk heating of an explosive can be described satisfactorily by solving the Frank-Kamenetskii equation with Arrhenius kinetics.

The shock initiation of detonation in nitromethane, liquid TNT, and single-crystal PETN may be described using Lagrangian reactive fluid dynamics with Arrhenius kinetics.

The process of detonation initiation and propagation of homogeneous explosives along surfaces can be described using Arrhenius kinetics. Since the reaction zone is orders of magnitude smaller than the scale of the experiments, most studies using numerical reactive fluid dynamics with Arrhenius kinetics are only qualitative.

References:

Basic

1. P. Gray and P.R. Lee, "Thermal Explosion Theory," in Oxidation and Combustion Reviews, edited by C.F.H. Tipper, Elsevier Publishing Company, New York, NY, 2, 1-185 (1967).

2. J. Zinn and C.L. Mader, "Thermal Initiation of Explosives," Journal of Applied Physics 31, 323 (1960).

3. D.A. Frank-Kamenetskii, "Calculation of Thermal Explosion Limits," Acta Physcochimica U.R.S.S. 10, 365 (1939).

4. A.W. Campbell, W.C. Davis, and J.R. Travis, "Shock Initiation of Detonation in Liquid Explosives," Physics of Fluids 4, 498 (1961).

5. C.L. Mader, "Shock and Hot Spot Initiation of Homogeneous Explosives," Physics of Fluids 6, 375 (1963).

C.L. MADER

Advanced

1. R.N. Rogers, "Thermochemistry of Explosives," Thermochimica Acta 11, 1341 (1975).

2. J. Zinn and R.N. Rogers, "Thermal Initiation of Explosives," Journal of Physical Chemistry 66, 2646 (1962).

3. T.I. Cottrell, T.E. Graham, and T.Y. Reid, "The Thermal Decomposition of Nitromethane," Transactions of Faraday Society 47, 584 (1951).

4. C.L. Mader, Numerical Modeling of Detonations, University of California Press (1979).

5. P. Persson and G. Persson, "High Resolution Photography of Transverse Wave Effects in the Detonation of Condensed Explosives," Sixth International Symposium on Detonation, ACR-221, 414 (1976).

6. I.M. Voskoboinikov, V.M. Bogomolov, A.D. Margolin, and A. YaApin, "Determination of the Decomposition Times of Explosive Materials in Shock Waves," Doklady Akademii Nauk, SSSR 167, 610 (1966).

7. J.R. Travis, "Experimental Observations of Initiation of Nitromethane by Shock Interactions at Discointinuities," Fourth International Symposium on Detonation, ACR-126, 386 (1965).

8. A.W. Campbell, W.C. Davis, J.B. Ramsay, and J.R. Travis, "Shock Initiation of Solid Explosives," Physics of Fluids 4, 511 (1961).

SHOCK PROPAGATION, DISSOCIATION, AND REACTION DYNAMICS IN COMPLEX TWO- AND THREE-DIMENSIONAL SYSTEMS

A.M. KARO*
Department of Chemistry and Materials
Lawrence Livermore Laboratory
Livermore, CA
U.S.A.
AND
J.R. HARDY
Department of Physics and Astronomy
University of Nebraska
Lincoln, NE
U.S.A.

ABSTRACT

We proceed in the third lecture to a discussion of diatomic and polyatomic lattices in two and three dimensions. In going from monatomic to complex structures we must consider the interaction of the energy localized in a shock front of atomic dimensions with the vibrational modes (phonons) of the material. We have already seen in treating the 2D defect problem that energy transfer is both a complex and important dissipative mechanism. In this lecture we sill review and focus on processes by which the "mechanical" type of energy imparted to a condensed material by shock loading is converted into the "activation" type of energy required to surmount the initial activation barrier along the reaction path.

A series of computer simulations studies of shock propagation in diatomic lattices will be discussed. The general nature of the computer codes we use allow an arbitrary specification of atomic and bond parameters, so that any desired structure can be built up on which to perform our computer experiments. The lattices we will now treat may contain voids, grain boundaries, and other point and line defects. The influence of such structural discontinuities and of the free surface itself on dissociation will be discussed. Complex substances such as the eneregetic material, pentaerythritol tetranitrate (PETN) can be modeled, and a simple 2D simulation study will be analysed, including the rather unexpected incubation behavior exhibited in the dynamics.

We conclude with a discussion of metastable lattices - a class of energetic systems in which under appropriate initiating conditions phase transformations can occur to configurations of greater

A.M. KARO

stability. Such studies can contribute to the understanding of
energy release behind the shock front and to the relationship of
the chemistry in the reaction zone to the characteristics of the
shock front itself.

A final movie will demonstrate the behavior of shock distur-
bances in complex lattices and in metastable systems.

References:

1. A.C. Scott, F.Y.F. Chu, and D.W. McLaughlin, Proc. IEEE 61,
    1443 (1973).

2. D.H. Tsai and C.W. Beckett, J. of Geophys. Res. 71, 2601
    (1966).

3. R. Manvi and G.E. Duvall, J. Phys. D. Ser. 2, 2, 1389 (1969).

4. R.A. MacDonald and D.H. Tsai, Phys. Reports 46, 2 (1978), and
    references contained therein.

5. L. Davison and R.A. Graham, Phys. Reports 55, 256 (1979), and
    references contained therein.

6. A.M. Karo and J.R. Hardy, Int. J. Quant. Chem. XII, Suppl. 1,
    333 (1977).

7. A.M. Karo, J.R. Hardy, and F.E. Walker, Acta Astronautica 5,
    1041 (1978).

THE CHARACTERIZATION OF AN ORDER-DISORDER PHASE TRANSITION IN A MOLECULAR CRYSTAL BY COMPUTER MOLECULAR DYNAMICS

S.F. TREVINO
Energetic Materials Division
LCWSL, ARRADCOM, Dover, NJ
and
National Bureau of Standards
Washington, DC
and
D.H. TSAI
National Bureau of Standards
Washington, DC
U.S.A.

ABSTRACT

We have recently begun a program designed for the investiga-
tion of the mechanisms by which energy released by a chemical reac-
tion redistributes itself in condensed matter. The general outline
of the work is as follows. We wish to model a diatomic molecule
which is capable of dissociation into a state of lower energy (thus
leading to a release of kinetic energy). This dissociation is
effected through the interactions with neighboring molecules. In
addition, we wish to allow recombination so as to better mimic
nature. For this purpose, a pairwise potential is constructed of
two parts, each a (6-12) type. The intermolecular potential whose
minimum corresponds to the larger distance is chosen as the
Lennard-Jones 12-6 potential. The intramolecular potential is
scaled in a somewhat arbitrary fashion and is given by:

$$\phi_{intra} = \frac{4\varepsilon}{n}\left[\left(\frac{\sigma}{nr}\right)^{12} - \left(\frac{\sigma}{nr}\right)^{6}\right] + \frac{\varepsilon}{2}$$

where ε and σ are the same parameters as in the Lennard-Jones
potential, and n is a scale factor. We have used $n=3$ and $n=4$.
Having thus defined the pairwise interaction of all the atoms,
computer molecular dynamics is used to obtain the response of a
collection of such particles to various stimuli. The initial step
in our investigation is the construction of a perfect crystal
modeled in the standard method by using periodic boundary condi-
tions of an array of diatomic molecules. The initial configuration
consists in placing the cente of mass of the molecule on an FCC
lattice and allowing them to relax until a stable orientational

configuration is obtained. This process led to a crystal structure very similar to that of N_2 in its lowest temperature phase with the single exception that the cell was slightly tetragonal (c/a = 0.97) rather than cubic. The crystal was heated while holding the volume constant and various properties were monitored. These included the total energy, the kinetic energy, the intramolecular distance, the single molecule angular correlation function $(G(\gamma) = \sum_n \int \delta(\gamma - \gamma_n) d\gamma$ where the sum is over the particles in the model and γ_n is the angle which the molecular axis makes with the z-axis, for example) etc. The initial intention of this experiment was to observe chemical decompositions. For this purpose, the intramolecular separation was carefully monitored. It was observed that, although the amplitude of the molecular stretch increased with temperature, the maximum separation of the two atoms of the molecule was never much larger than the distance to the minimum of the first potential. Our interpretation of this result is that in a perfect crystal lattice, decomposition is greatly hindered by the presence of neighboring molecules; and in addition, that increasing the pressure on the system also inhibits decomposition. It is clear to us from this that the role of defects (vacancies) is of crucial importance to the mechanisms of decomposition in the solid. It is our intent to study these details with our model. As the heating was continued, a lambda type order-disorder phase transition was detected. The transition is characterized by a pronounced continuous increase in internal energy as a function of temperature and in the width of $G(\gamma)$ as a function of γ until at just above the transition temperature $G(\gamma)$ is essentially a constant with γ. Upon cooling, the ordering transition exhibited substantial hypteresis, but the original crystal structure (with a few orientational defects) was recovered. A complete characterization of this phase transition will be presented. To our knowledge, this is the first successful model on an atomic scale which exhibits this interesting phase transition.

FAST PERFORMANCE IN NONIDEAL EXPLOSIVES*

I.B. AKST
Idos Corporation
Pampa, TX
U.S.A.

ABSTRACT

Performance data from eutectic intermolecular explosives are presented showing that fast reactions in nonideal explosives can be produced, yielding prompt energy and early metal accelerating performance similar to that produced by ideals.

Using the data to demonstrate that metal-propulsion ability can vary independently of chemical energy and the CJ parameters of detonation pressure and velocity, the effect of several other ordinary factors is postulated. These are the amount of detonation product gas, its molecular weight, detonation temperature, and condensation kinetics of solid products. The suggestion is made that these factors need more study, to learn how to calculate or even measure them.

COHERENT ANTI-STOKES RAMAN SPECTROSCOPY
OF GUN PROPELLANT FLAMES

L.E. HARRIS*
Propulsion Technology
Large Caliber Weapon Systems Laboratory
ARRADCOM, Dover, NJ
U.S.A.
AND
M. McILLWAIN
Geo-Centers, Inc.
381 Elliot St.
Newton Upper Falls, MA 02164
U.S.A.

ABSTRACT

Measurement of temperature and concentration profiles in propellant flames should provide some of the data needed to unravel the controlling mechanisms of propellant combustion. These measurements are exceedingly difficult to make using conventional optical methods since propellant flames are transitory with interferences due to flame incandescence and scattering due to particulate matter.

A new spectroscopic technique based on the generation of Coherent Anti-Stokes Raman scattering (CARS) through the nonlinear interaction of two high intensity laser beams with the sample provides a means of probing propellant flames. The high intensity, spacial resolution (1MM), and time duration (10ns) of the CARS signal makes propellant flames studies possible.

The first CARS spectra obtained from propellant flames will be reported. These spectra were obtained using a repetitively pulsed Nd/YAG laser both as one of the incident beams and to pump a broadband dye laser to provide the other incident beam. Detection of the CARS signals, which were generated within the duration of the incident laser pulses was accomplished using a monochromator coupled to an optical multi-channel analyser. These CARS spectra were generated from nitrogen present in the propellant flame. Sufficient spectral resolution was obtained to allow determination of the propellant flame temperature from the propellant CARS spectra. The temperature is determined by modeling the temperature dependent CARS spectra. The model utilized involves use of a boltzmann distribution over the spectroscopic ro-vibrational levels to calculate the nonlinear third order susceptibility. The third

L.E. HARRIS

order susceptibility is then convoluted over the spectral distributions of the incident beams with appropriate corrections for the monochromator slit function to generate the CARS spectra.

The results obtained confirm the potential utility of CARS for mapping temperature profiles and the concentration profiles of the major species in propellant flames. The relation of the results obtained to current propellant combustion models will be discussed.

HIGH TEMPERATURE, HIGH PRESSURE KINETICS
IN EXPLOSIVE LIQUIDS

C.M. LOWNDS
Detonation Research Group
ICI Corporate Laboratory
Stevenston Works, Ayrshire
Scotland, KA20 3LN

ABSTRACT

A short, nontheoretical paper describing a technique for obtaining kinetic data on ignition of reactive liquids: pressures at present achieved are 5 kbar with the hope of extension to 20 kbar, and the temperature range is 600 to 1500 K. Results will be presented on the ignition under these conditions of nitromethane and aqueous hydrazine mononitrate solutions. The method yields Arrhenius parameters for the ignition process in exothermic liquids.

Reference:

1. C.M. Lownds, "Prediction of the Performance of Explosives in Bench Mining," Journal of the South African Institute of Mining & Metallurgy, Vol 75, No. 7, pp 165-81 (Feb 1975).

LASERPYROLYSIS OF HIGH ENERGETIC MATERIALS

A. PFEIL* AND N. EISENREICH
Fraunhoferinstitut für Treib- und Explosivstoffe
D-7507 Pfinztal 1
West Germany

ABSTRACT

High energetic materials like nitrocellulose and solid propellants were thermally excited by a pulsed ruby laser and the fast thermal degradation process studied by high speed photography, emission spectroscopy, TOF and MS. Of interest were the interaction process of the laser pulse with the high energetic material and the nature of the decomposition products.

To characterize the interaction process the pyrolysis craters were discussed on the basis of a three-dimensional heat flow equation assuming an infinitesimal short heat source. The experimental crater dimensions were correlated with the laser pulse energy and the pyrolysis temperature of the solid.

MS analysis of the plume confirms the presence of products typical for primary decomposition reactions. In the plume emission spectrum the continuous emission background and, for example, the bands of OH and CuH, characteristic for propellant flames, are absent. TOF and emission spectra distinctly show the influence of additives for faster and more energetic reactions like ballistic modifiers on the composition of the plume.

HIGH DENSITY EXCITATION CALCULATIONS
IN MOLECULAR SOLIDS: A MONTE CARLO STUDY

BY

P. ARGYRAKIS*, J. HOSHEN AND R. KOPELMAN
Department of Chemistry
The University of Michigan
Ann Arbor, MI
U.S.A.

ABSTRACT

The effects of the creation of a high flux of excitation via continuous wave and pulsed light sources are studied. We employ ternary molecular periodic lattices with given pairwise interactions containing high energy scattering sites and low energy trap sites. We investigate the rates of exciton-exciton annihilation, trapping, and decay of excitation as a function of the light intensity, all three component concentrations, and the lifetime of excitation. These simulations are compared with experimental results on naphthalene systems.

TIME-RESOLVED RESONANCE RAMAN SPECTROSCOPY OF FREE RADICALS AND EXCITED STATES IN PULSE RADIOLYSIS

R. WILBRANDT*, N.H. JENSEN, A.H. SILLESEN
AND P. PAGSBERG
Risø National Laboratory
DK - 4000 Roskilde, Denmark

ABSTRACT

The technique of resonance Raman spectroscopy (RRS) of short-lived intermediates as free radicals and excited states has recently developed to a powerful and specific analytical tool for the study of fast chemical reactions (1). It involves pulsed laser excitation and optical multi-channel detection of scattered light and enables to obtain detailed vibrational information on species at $10^{-6} - 10^{-4}$ molar concentrations.

Applications are presented where RRS is combined with the method of pulse radiolysis. The lowest excited triplet state of all-trans β-carotene and related compounds is produced by irradiation of a solution of the latter in benzene with a pulse of high energy electrons. The resonance Raman spectrum of the triplet excited state is presented and compared with that of the ground state. Previous findings (2) are confirmed and vibrational bands not yet reported are discussed.

References:

1. K.B. Hansen, R. Wilbrandt and P Pagsberg, Rev. Sci. Instr. 50, 1532 (1979) and references therein.

2. R.F. Sallinger, J. J. Guanci, Jr., W.H. Woodruff and M.A.J. Rodgers, J. Am. Chem. Soc. 101, 1355 (1979).

RELIABLE AB-INITIO QUANTUM CHEMICAL CALCULATIONS ON ENERGETIC SPECIES

J.J. KAUFMAN
Department of Chemistry
The Johns Hopkins University
Baltimore, MD
U.S.A.

Processes of significance in depicting the bond breaking energies, excited states, decomposition pathways and reactive pathways of energetic species can only be delineated reliably by high quality ab-initio quantum chemical calculations including electron correlation effects. Even the electronic structures of the ground states of the molecules themselves are more accurately depicted by good quality ab-initio SCF calculations as are properties subsequently calculated from these ab-initio SCF wave functions than from any less rigorous quantum chemical procedures.

The state-of-the-art is now such that it is possible to carry out ab-initio calculations [SCF, MC-SCF (multiconfiguration SCF) and CI (configuration interaction)] calculations on molecules of the size of interest even for substituted heterocyclic explosives. In our group we have over the past few years added to our own efficient ab-initio integral and SCF programs a number of desirable options for calculations on large molecules: the use of ab-initio effective core model potentials (MODPOT) which permit calculation of valence electrons explicitly, yet accurately; a charge conserving integral prescreening evaluation especially effective for spatially extended molecules; an efficient MERGE technique which permits reuse of common skeletal integrals; a new SCF technique to take advantage of common Fock matrix element contributions from common skeletons up until just before convergence; plus implementing for CI a technique allowing folding into an effective CI Hamiltonian the effect of molecular orbitals from which excitations are not allowed (thus obviating the necessity for the computer time- and space-consuming transformations from integrals over atomic orbitals to integrals over molecular orbitals); and meshing in an open ended transformation program allowing transformation over extremely large basis sets.

A brief overview of the merits and deficiencies of various quantum chemical calculational procedures will be given. Recent examples of our calculations on energetic species including

J.J. KAUFMAN

electrostatic molecular potential contour maps to understand
propensities for cationic polymerization of energetic monomers to
make energetic binders will be presented.

Acknowledgement:

CHEMICAL PATHS IN THE SHOCK INITIATION OF DETONATION.
A THEORETICAL STUDY

J. ALSTER
Energetic Materials Division
LCWSL, ARRADCOM, Dover, NJ
U.S.A.

ABSTRACT

Past studies of shock initiation of detonation in explosives are based primarily on a thermohydrodynamic, continuum model. This paper attempts to explain some shock-hydrodynamic observations in terms of molecular interactions. In particular, decomposition pathways for the explosive molecule are explored theoretically. Semiempirical quantum-chemical calculations are employed in selecting energetically preferred paths for both unimolecular and bimolecular decomposition of the explosive molecule. As different reaction paths lead to widely different primary decomposition species, their possible influence on growth of initiation-to-detonation is explored.

General References:

1. G.A. Segal, editor, "Semiempirical Methods of Electronic Structure Calculations," Part A: Techniques; Chapter 2. G. Klopman and R.C. Evans, "The Neglect-of-Differential-Overlap Methods of Molecular Orbital Theory," Plenum Press, New York, NY (1977).

2. G.A. Segal, editor, "Semiempirical Methods of Electronic Structure Calculation," Part B: Applications; Chapter 1. M.C. Flanigan, A. Komornicki and J.W. McIver, Jr., "Ground State Potential Surfaces and Thermochemistry," Plenum Press, New York, NY (1977).

3. G.A. Olah and P. von R. Schleyer, editors, "Carbonium Ions," Volume 5; Chapter 35. L. Random, D. Poppinger and R.C. Haddon, "Molecular Orbital Theory of Carbocations," John Wiley & Sons, Inc., New York, NY (1976).

4. M.J.S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw Hill, Inc., New York, NY (1979).

J. ALSTER

Specifi References:

1. R.C. Bingham, M.J.S. Dewar and D.H. Lo, "Ground States of Molecules. XXV, MINDO/3. An Improved Version of the MINDO Semiempirical SCF-MO Method," J. Am. Chem. Soc., 97, 1302 (1975).

2. R.C. Bingham, M.J.S. Dewar and D.H. Lo, "Ground States of Molecules. XXVII. MINDO/3 Calculations for CHON Species," J. Am. Chem. Soc., 97, 1302 (1975).

3. M.J.S. Dewar and S. Olivella, J. Am. Chem. S'.:., 100, 5290 (1978).

4. M.J.S. Dewar, "Studies of the Mechanisms of Some Organic Reactions and Photoreactions by Semiempirical SCF MO Methods," Far. Disc. of the Chem. Soc, 62, 197 (1977).

5. M.J.S. Dewar, "Quantum Organic Chemistry," Science, 187, 1037 (1975).

6. M.J.S. Dewar, "Computing Calculated Reactions," Chem. in Britain, 11, 97 (1975).

EXPERIMENTAL ION-MOLECULE DYNAMICS
INCLUDING REACTIONS INVOLVING EXCITED STATES

W.S. KOSKI
Department of Chemistry
The Johns Hopkins University
Baltimore, MD
U.S.A.

ABSTRACT

The scattering of ions in their ground and first excited states by simple molecular targets have been studied in our laboratory.

In the reactive scattering of $B^+(^1S_g)$ and $B^+(^3P_u)$ by molecular deuterium to produce

$$BD^+(^2\Sigma^+) \text{ and } BD^+(^2\Pi)$$

the angular and energy distribution of the ionic products were measured and used to deduce mechanistic information about the reactions. The limiting values of the translational exoergicities were used to determine product states and the distribution of energy between the internal and translational degrees of freedom.

In a corresponding study of the reaction of C^+ with H_2 and D_2 the collisional conditions were favorable and the instrumental resolution good enough to resolve vibrational structure in the product ion (CH^+) energy spectrum over a range of projectile ion energies. The energy spectrum also permitted the identification of product ions in various electronic states.

Finally the collisions between halogen ions (Cl^+ and Br^+) with Ar and Kr were studied. It was found that an efficient mechanism of transferring electronic energy of excitation from the halogen ion into translational energy of the rare gas and vice versa exists.

All of these studies were carried out under single collision conditions.

COUPLING OF MOLECULAR TO LATTICE VIBRATIONAL MODES
IN ENERGETIC SOLIDS:
RAMAN SPECTROSCOPIC STUDIES

Z. IQBAL
Institute of Inorganic Chemistry
University of Zürich
8057 Zürich, Switzerland

ABSTRACT

In this talk I will discuss the Raman scattering response in two materials which are known to explode on the application of external fields such as shock, stress and varying temperature. The first is a largely ionic solid, namely thallium azide (TlN_3) and the second is a molecular crystal, tetrasulfur nitride (S_4N_4), which consists of 8-membered S_4N_4 rings. In TlN_3 the Raman response shows that two modes: one a libration localized on the N_3^- sites and the other a shearing motion involving both the cation and anion sublattices, are strongly coupled. The consequences of this coupling and the possible role of the N_3^- bending mode in this scheme will be discussed. In the van der Waal-type S_4N_4 lattice, the intermolecular and molecular modes show evidence of weak coupling. A librational mode, however, shows a rapid drop in frequency as the melting point of S_4N_4 (near which S_4N_4 appears to decompose explosively), is approached. This result is interpreted in terms of vibrational frequency renormalization with temperature which occurs as a consequence of mode anharmonicity.

References and suggested readings:

1. C.W. Christoe and Z. Iqbal, J. Phys. Chem. Solids 38, 1391 (1977); Z. Iqbal, C.W. Christoe and D.S. Downs, Ibid 38, 263 (1977).

2. Z. Iqbal in Magnetic Resonance of Phase Transitions (Ed. F.J. Owens, et al.) Chap 1, Academic Press, New York, NY (1979).

3. J.F. Scott, Reviews of Modern Physics 46, 83 (1974).

ADIABATIC RATE PROCESSES IN CONDENSED MEDIA

B. FAIN
Department of Chemistry
Tel-Aviv University
Tel-Aviv, Israel

ABSTRACT

A model describing adiabatic transitions in condensed media is developed. The model may be appropriate for the description of nuclear group transfer of nuclear groups or transition between two stable configurations of a molecule embedded in condensed media. Both high and low temperature behavior are analyzed. It is shown that at low temperatures $kT \ll h\omega_0$, where $h\omega_0$ is the characteristic difference in the potential wells, the model is isomorphous to a well explored theoretical model with two intersecting electronic energy hypersurfaces.

At temperatures $kT \gg h\omega_0$ the rate equations describing the overcoming of the barrier between the potential wells by the excitations of the surrounding media are derived.